

"High pressure behavior of Ga-doped LaMnO_3 : a combined X-ray diffraction and optical spectroscopy study."

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The pressure effects on the JT distortion of three representative compounds belonging to the $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ ($x = 0.2, 0.3, 0.4$) family was widely investigated by means of X-ray diffraction and Raman spectroscopy. A compound with a fully JT distorted structure ($x=0.2$), one with regular octahedra ($x=0.6$) and one in an intermediate configuration ($x=0.3$) were selected. A pressure induced transitions from the orthorhombic $Pbnm$ phase towards structures with higher symmetry were observed in all the samples. Both Raman and X-ray data confirm that the most important structural effect of pressure is that of reducing the octahedral distortion. The appearance of a feature in the lattice parameter behavior connected to a structural instability was also detected, pointing out the key role of the JT distortion in stabilizing the manganite structures. On the other hand, the complete suppression of the JT distortion in the high-pressure phases cannot be claimed. The Raman spectra collected from more distorted compounds ($x=0.2, 0.3$) reveal clearly the coexistence of domains of distorted and more regular octahedra in a certain pressure range. The first sketch of the Pressure vs. Ga-content phase diagram was drawn.

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I. INTRODUCTION

In recent years large efforts have been devoted to the comprehension of the fundamental mechanisms involved in the charge doped colossal magnetoresistance manganites [1]. Theoretical and experimental results show the close correlation between structural, orbital, and electronic degrees of freedom, which have to be taken into account to shed light on the complex physics underlying the unique properties of these compounds. In particular, the orthorhombic parent compound LaMnO_3 is considered as the prototype of a *coherent* Jahn-Teller (JT) system, where a cooperative tetragonal deformation of the MnO_6 octahedra occurs [2]. The LaMnO_3 structure can be viewed as a sequence of alternate short and long Mn-O bonds in the ab plane [3]. Furthermore, the occurrence of d -type orbital ordered state [4, 5], which plays a fundamental role in stabilizing the anisotropic A-type antiferromagnetic state, has also been clearly pointed out [2, 6, 7]. The replacement of trivalent La with a divalent ion (Ca, Sr) corresponds to an effective hole-doping. In the $0.2 < x < 0.5$ concentration range, colossal magnetoresistance [8] and a ferromagnetic metallic ground state are observed, which are qualitatively well explained by means of the double exchange (DE) mechanism [9]. Although the above picture appears to be rather well established, recent investigations carried out on Ga^{3+} doped compounds have opened up new interesting, and still unsolved, questions. Indeed, the replacement of Mn^{3+} by a nonmagnetic and non Jahn-Teller (JT) ion like Ga^{3+} , surprisingly induces a ferromagnetic insulating ground state in the $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ compounds for $0.4 \lesssim x \leq 0.6$

[10]. It is worth noticing that the absence of hole-doping in these compounds does not allow to ascribe this singular behavior to a DE mechanism. All the structural studies on this family of compounds [10, 11, 12] show that the Ga substitution progressively reduces the JT distortion leading, for $x \geq 0.6$, to a crystallographic structure with all the MnO_6 octahedra in a symmetric configuration. The behavior of magnetization can be described by a spin-flipping model: this theoretical result seems to suggest that the Ga doping, by removing the JT distortion, perturbs the orbital order and favors the ferromagnetic ground state [13]. On the other hand, Raman and X-ray diffraction experiments previously performed on the parent compound have suggested that the cooperative JT effect in LaMnO_3 [14] can be reduced by application of hydrostatic pressure. Therefore, hydrostatic pressure, coupled with Raman spectroscopy and X-ray diffraction, turns out to be a very effective tool to investigate the role of the JT distortion [14] in the Ga doped LaMnO_3 . A recent Raman experiment [15], performed on several compounds of the $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ family ($0.1 < x \leq 0.8$) confirms the removal of the JT octahedra distortion on increasing the Ga doping. Moreover, high pressure Raman measurements performed on the $x = 0.2$ (LG20) and $x = 0.6$ (LG60) samples have revealed that pressure, as well as doping, favors the symmetrization process [15]. However, differences between the doping and pressure effects have been also pointed out by these Raman measurements [15].

In the present paper, a deeper and more extended investigation of the pressure effects on the JT distortion [14] in the Ga doped LaMnO_3 has been carried out. In

particular high pressure X-ray diffraction measurements were carried out over the 0 – 18 GPa pressure range on three Ga doped manganites at room temperature, namely the $x = 0.2$ (LG20), $x = 0.3$ (LG30) and $x = 0.6$ (LG60) compounds. A new high-pressure Raman measurement (0 – 13 GPa) has been also carried out on the LG30 sample in order to have, together with the data reported in Ref. 15, a complete set of high-pressure Raman and X-ray diffraction data for the LG20, LG30, and LG60 samples. These compositions have been chosen since a fully *JT* distorted structure is observed in the LG20 sample, opposite to the symmetric regular octahedra observed in the LG60 compound, whereas the LG30 sample is in an intermediate configuration. Both the experimental techniques show that hydrostatic pressure is an effective tool in order to reduce the *JT* distortion. The pressure induced reduction of *JT* distortion is clearly observed by both Raman and X-ray measurements. On the other hand, the pressure induced symmetrization process turn out to be different from that induced by doping.

II. EXPERIMENTAL

The $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ samples (LG20, LG30 and LG60) were prepared following a conventional ceramic procedure [10]. Stoichiometric amounts of La_2O_3 , MnCO_3 , and Ga_2O_3 were mixed, milled, and fired at 1250 °C during 24 h in air. Then, the resulting powders were milled, pressed into pellets and sintered at 1250 °C for another 24 h in air. Finally, the pellets were milled, repressed and sintered at 1400 °C for 48 h in an argon atmosphere. The oxygen content of the samples was analyzed using standard redox titration with KMnO_4 and Mohr's salt. These samples were oxygen-stoichiometric, within the analysis accuracy ± 0.02 [10].

High pressure X-ray diffraction data were collected on the ID27 beamline at the ESRF Facility in Grenoble, which is dedicated at high pressure diffraction experiments. The beam ($\lambda = 0.41 \text{ \AA}$) size on the sample is normally about $30 \times 30 \text{ }\mu\text{m}^2$. A membrane diamond anvil cell (MDAC) equipped with low fluorescence IIA, 400 μm culet diamonds has been used. The samples were finely milled and an high-pressure MDAC-loading with N_2 , as pressure transmitting medium was performed. The image plate detector is a Mar345 reader. The experimental line width in the diffraction pattern is smaller than $\Delta\theta = 0.05$ FWHM (Full Width at Half Maximum). The X-ray data were refined by means of the Fullprofile software [16].

Raman spectra were measured in back-scattering geometry, using a micro-Raman spectrometer (LABRAM by Jobin Ivon) with a charge-coupled device (CCD) detector and an adjustable notch filter. The samples were excited by the 632.8 nm line of a 15 mW He-Ne Laser. The confocal microscope was equipped with a 20X magnification objective which gives laser spot about $5\text{ }\mu\text{m}^2$ wide at the sample surface. The Raman spectra were collected in the 200-1100 cm^{-1} frequency range. The MDAC was

equipped with low fluorescence IIA diamonds with 800 μm culet diameter. The hydrostatic conditions for the sample were ensured by the NaCl salt loaded with the sample. Moreover, owing to the high thermal conductivity of diamond, spurious effects due to laser-induced sample heating can be prevented [17]. Since the laser spot size ($5 \text{ }\mu\text{m}^2$) is much smaller than the sample diameter size ($200 \text{ }\mu\text{m}^2$) we were able to collect Raman spectra from three different points of the sample. A good spectral reproducibility of the spectra was obtained at each pressure. The spectra from different zones were analyzed separately using a DHO function [17] and the best fit parameters were averaged. The pressure measurement is obtained, in both the experimental techniques, exploiting the standard ruby fluorescence technique [18].

III. EXPERIMENTAL RESULTS AND DISCUSSION

The $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ compounds belong to the family of oxides with a perovskite-like structure. At ambient pressure the samples show an orthorhombic *Pbnm* structure. Two orthorhombic *Pbnm* phases can be distinguished: the first, usually named O', is observed for $x \leq 0.5$ and it is related to a *JT coherent* deformation of the MnO_6 octahedra and to orbital ordered state; the other one, named O, is observed for $x > 0.5$ and it is related to regular octahedra and to an orbital disordered phase [10, 11, 12]. The three presently investigated samples thus belong to both the phases and namely LG20 and LG30 to the O' phase, and LG60 to the O one.

A. High pressure X-ray diffraction

Figure 1 reports the X-ray diffraction patterns collected on the LG20, LG30 and LG60 samples at the lowest pressure. The Rietveld refinements performed on these patterns are in good agreement with the O' (LG20 and LG30) and O (LG60) *Pbnm* phases reported in literature [10]. The disappearance of the (0 2 0), (2 0 2), (0 0 4) and the (3 1 2) reflections with doping (see Fig.1) marks the structural transition from the *JT* distorted O' to the undistorted O *Pbnm* phase, previously reported in ref. [10].

In Fig.2 the diffraction patterns of the three samples collected at selected pressures are shown. In all the measured samples, the lattice compression induces a clear shift of the diffraction peaks towards higher angles as the pressure is increased. At a first glance, the appearance of new diffraction peaks is observed in the LG20, LG30 and LG60 diffraction patterns collected at the highest pressure, which can be associated to a pressure induced structural transitions. The clear peak splitting of the reflection centered at around 15° (see the black arrow in Fig.2 (a), (b) and (c)), marks well the onset of the structural transition in all the samples.

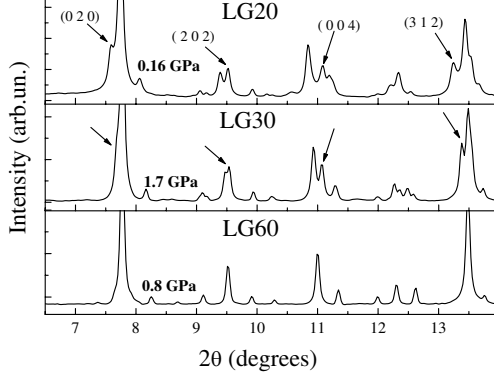


FIG. 1: X-ray diffraction patterns collected at the lowest pressure. The black arrows indicate the (0 2 0), (2 0 2), (0 0 4) and the (3 1 2) reflections which are the marker of the structural transition from the O' to the O phase.

All the patterns were analyzed with the Rietveld method. The change in the peak intensities together with the peak spreading, both induced by pressure, do not allow to extract trustworthy information from the atomic position refinements, thus only the pressure dependence of the lattice parameters, is reported in this paper. The results are shown in Fig.3 (LG20 and LG30) and in Fig.4 (LG60). As the pressure is increased, structural transitions are observed in all the measured compounds. A transition from an orthorhombic $Pbnm$ O'-type to an orthorhombic $Imma$ phase occurs at around 12 GPa in the LG20 sample, and a transition from orthorhombic to rhombohedral $R\bar{3}c$ phase is observed at around 10 and 7 GPa in the LG30 and LG60 compounds, respectively. The onset of the higher symmetric orthorhombic $Imma$ and the rhombohedral $R\bar{3}c$ space groups indicates that pressure really promotes the octahedra symmetrization. However more detailed information can be deduced by the lattice parameter pressure behavior. It is worth to notice that the onset of *coherent JT* distortion in the $Pbnm$ symmetry lowers the $a/\sqrt{2}$ ratio and yields $c/\sqrt{2} < a < b$ [19]. Therefore, in the orthorhombic structure $Pbnm$, if the c parameter is smaller than a and b , the occurrence of an orbital ordering can be hypothesized [20]. Moreover, since the *JT* distortion mainly affects the Mn-O distance in the ab plane, changes in the b cell parameter can be a good indicator of the magnitude of the cooperative *JT* distortion [20]. Within the O' phase both LG20 and LG30 samples show the b pressure rate of compression larger than that of the a and c parameters so that a crossing of the a and b lattice parameters occurs at around 8 GPa (LG20) and 6 GPa (LG30). This finding is once more compatible with a pressure-induced reduction of the *JT* distortion in both the samples. Above the transition pressure ($P=12$ GPa) three distinct lattice parameters are still observed in LG20 ($Imma$ phase) and the values of the c parameter keep smaller than those of

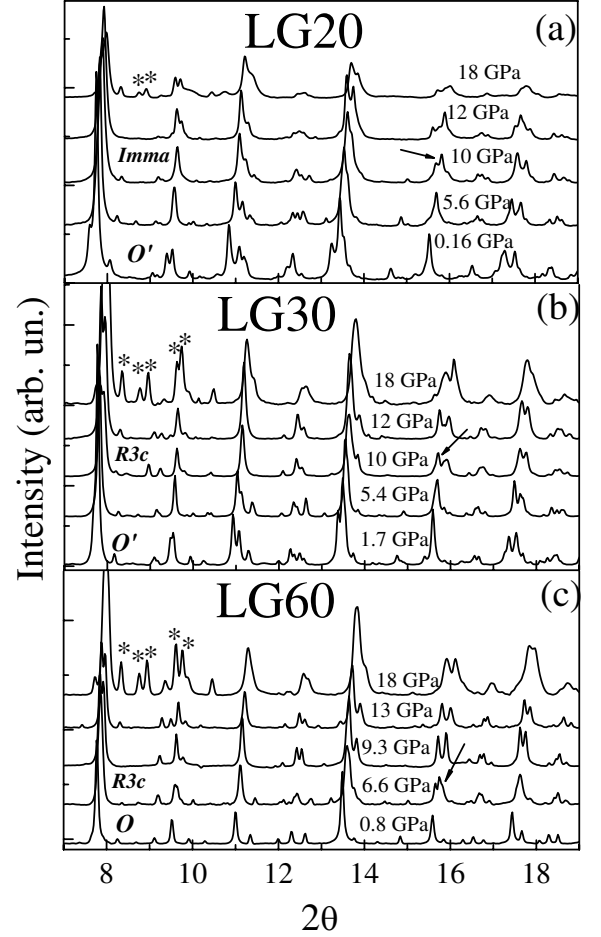


FIG. 2: Diffraction patterns of LG20 (a), LG30 (b) and LG60 (c) samples at selected pressure. The black arrow indicates the peak splitting occurring at the structural transition. The asterisks mark the reflections due to the nitrogen pressure medium in the ϵ -phase.

the b and the a parameters. These findings thus suggest, that the pressure-induced removal of *JT* is not completed and that the persistence of a residual distortion also in the $Imma$ high pressure phase may be conjectured. On the other hand, the occurrence of only two Mn-O distances in the $Imma$ structure instead of the three ones characteristic of the O' phase is an indication of the loss of *coherence* of the octahedral deformation.

Above about 10 GPa LG30 enters the $R\bar{3}c$ phase where the occurrence of *coherent JT* distortion is not allowed owing to the rhombohedral tilting [20]. Nevertheless the presence of *dynamic* or *static incoherent JT* distortions, previously claimed in several $R\bar{3}c$ manganite compounds [21], cannot be ruled out. The data analysis of the two sample (LG20 and LG30) thus coherently indicates that the reduction of the *JT* distortion is promoted by hydrostatic pressure although a complete removal of octahedral distortion cannot be claimed.

At variance from the LG20 and LG30, the lattice param-

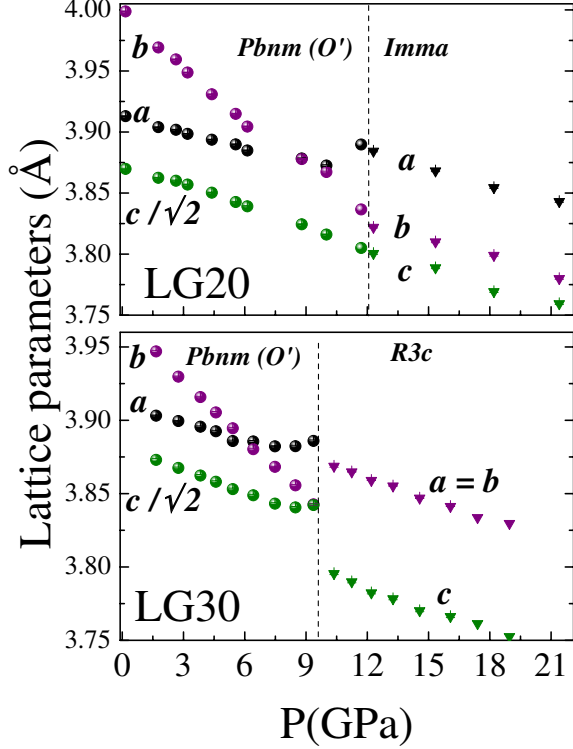


FIG. 3: Pressure dependence of the LG20 and LG30 lattice parameters. Vertical dashed lines mark the transition pressure.

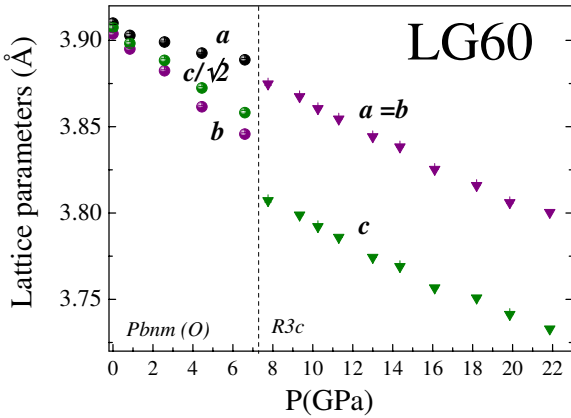


FIG. 4: Pressure dependence of the LG60 lattice parameters.

eters of LG60 are almost coincident at ambient pressure (see Fig.4) and show a peculiar pressure behavior. This is not surprising since LG60 at ambient pressure shows undistorted octahedra within the orthorhombic $Pbnm$ O-type ($a > b \simeq c/\sqrt{2}$) phase, whereas both LG20 and LG30 are characterized by JT distorted within the $Pbnm$ O'-

type phase. On applying pressure, the three LG60 lattice parameters get more and more distinct up to 7 GPa when a transition to the $R\bar{3}c$ phase occurs and only two lattice parameters are necessary to fit the diffraction data. We notice that although the values of lattice parameters, actually identical at ambient pressure distinguish each other as the pressure is increased over the 0-7 GPa pressure range, the ratio between the a , b , c lattice parameters suggests the absence of JT distortion until the $Pbnm$ is preserved [19]. In the high pressure regime ($P > 7$ GPa) the $R\bar{3}c$ phase does not allow the presence of *coherent* JT distortions as mentioned above, but in this case where the compound shows regular octahedra even at ambient pressure, the presence of *dynamic* or *static incoherent* JT distortions is very unlikely.

The crossing of the b and a lattice parameters, observed in both LG30 (at $P=6$ GPa) and LG20 (at $P=8$ GPa) deserves further discussion. This feature has been already observed in the pressure dependence of LaMnO_3 lattice parameters at around 10 GPa [14], and previously observed in the evolution of several AMnO_3 manganites lattice parameters as a function of the rare earth (A) ionic radius [20, 22], i.e., as a function of the chemical pressure. The crossover of b and a , as the ionic radius increases above 1.11 \AA , points out a structural instability in the orthorhombic $Pbnm$ O symmetry which leads to a structural transition from orthorhombic to rhombohedral ($R\bar{3}c$) phase [22]. It seems to be a general phenomenon, occurring during the symmetrization process, that systematically prevents a continuous evolution from the orthorhombic to the cubic AMnO_3 perovskite structure [22]. The a - b crossing observed in the Ga doped compounds and in LaMnO_3 [14], as the pressure is increased, could be ascribed to the same process. First of all this crossing is a clear mark of the octahedra symmetrization and the whole of our results are consistent with this statement. Indeed, by comparing the pressure behavior of the lattice parameters of the distorted LG20 and LG30 samples, the crossing occurs at a pressure threshold which is higher in LG20 ($P=8$ GPa) than in the less distorted LG30 ($P=6$ GPa) which shows weaker JT distortion and closer a and b parameters values. Consistently the a - b crossing does not occur in LG60 where the JT distortion is already removed and regular octahedra are already observed at ambient pressure. Moreover this result not only points out the connection between this feature and the reduction of JT distortion but it also gives a strong indication of the a structural instability occurring in the system. This instability is the precursor of a structural transition and prevents the direct evolution from a distorted to an undistorted cubic structure. Therefore, the pressure induced symmetrization process appears to occur step by step, through subsequent transitions to higher symmetry phases.

Some information on the orbital order state can be also indirectly deduced from the lattice parameter behavior. As mentioned above, in the orthorhombic structure $Pbnm$, if the c parameter is smaller than a and b , the

occurrence of an orbital ordering can be hypothesized [20]. Therefore, the occurrence of an orbitally ordered state can be reasonably supposed as long as the system preserves the orthorhombic O' $Pbnm$ phase in the LG20 and LG30 samples (see Fig.3). As to LG20 a clear understanding relative to the existence of an orbitally ordered state above the structural transitions is far to be completely achieved. In this case the c behavior above 12 GPa suggests the existence of some kind of orbital orientations in the LG20 $Imma$ high pressure phase. Similar problem was discussed for the LaMnO_3 in the high pressure regime ($P > 15$ GPa) [23]. A mixture of a -type and d -type JT distortion and thus of a and d -type orbital configurations was supposed in the LaMnO_3 high pressure phase [23]. This hypothesis is consistent with the results obtained in the LG20 sample. Indeed, it requires the loss of the JT distortion *coherence*, which results in the $Imma$ phase. However, the appearance of a specific orbital order configuration cannot be inferred and the hypothesis of an orbital disordered state cannot be ruled out.

The existence of an orbital ordered state is not allowed in the high pressure R_3c phase observed in both LG30 and LG60. Therefore, in the LG30 compound the occurrence of the d -type orbitally ordered state can be supposed only below 10 GPa. On the contrary, in the LG60 sample the occurrence of an orbitally ordered state can be also certainly ruled out over the whole pressure range. Indeed, c is larger than b in the $Pbnm$ O phase (see Fig.4), revealing an orbitally disordered state.

The pressure dependence of the cell volumes was calculated for each samples, and shown in Fig.5. The cell vol-

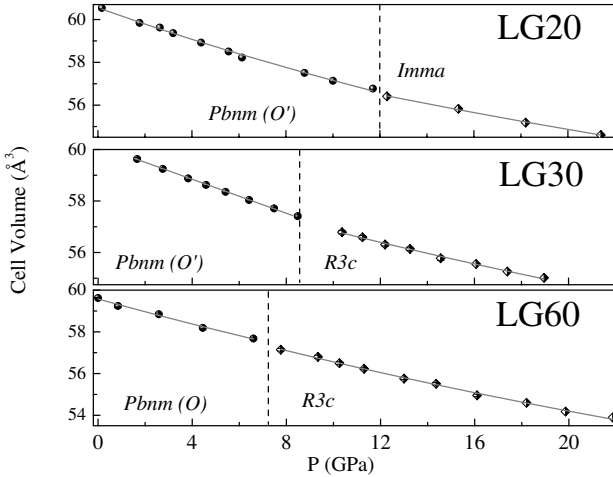


FIG. 5: Pressure dependence of the cell volumes. The experimental data (circles) was fitted with a Birch-Murnaghan curve (black line).

ume behavior as a function of pressure is well described by a Birch-Murnaghan curve [24, 25], which correlates the pressure to V/V_0 (V_0 is the cell volume at ambient

pressure) as follows:

$$P = \frac{K_0}{K'_0} \left[\left(\frac{V_0}{V} \right)^{K'_0} - 1 \right] \quad (1)$$

The bulk modulus K_0 , which characterizes the stiffness of the solid, was obtained below and above the structural transitions, whereas the derivative of the bulk modulus was fixed at $K'_0=4$ i.e. the typical value for crystals with nearly isotropic compression [14]. The best-fit curves obtained using the Birch-Murnaghan are in good agreement with the experimental results, as shown in Fig. 5. The best-fit values for K_0 for all the samples obtained in the low- and high-pressure phases are shown in Tab. I, where a summary of the main results discussed up to now is also reported. As to the low-pressure phases, we notice

LOW-PRESSURE PHASE			
sample	phase	Orbital ordering	K_0
LG20	$Pbnm$ O'	d -type	153 GPa
LG30	$Pbnm$ O'	d -type	160 GPa
LG60	$Pbnm$ O	no	188 GPa
HIGH-PRESSURE PHASE			
sample	phase	Orbital ordering	K_0
LG20	$Imma$?	209 GPa
LG30	R_3c	no	210 GPa
LG60	R_3c	no	175 GPa

TABLE I: K_0 values obtained by Birch-Murnaghan fit and the main results

that the K_0 value of the orbital disordered LG60 is about 20% larger than those of the orbital ordered LG20 and LG30. This result suggests that the stiffness of the solid increases in the undistorted and orbital disordered state. Bearing in mind this suggestion, some conjectures can be drawn about orbital ordering in the high-pressure phases. Indeed, we notice that the LG20 and the LG30 K_0 values remarkably increase (about 30 %) on entering the $Imma$ and the R_3c phases and get closer to the undistorted orbital disordered LG60 low-pressure value. These arguments may sustain the hypothesis that a specific orbital order configuration does not occur in the LG20 $Imma$ phase as well as in the LG30 R_3c one. On the other hand, the LG60 bulk modulus shows a different pressure behavior as it slightly decreases at high pressure. This can be explained, taking into account that the LG60 sample is undistorted and orbital disordered in both low- and high-pressure phases.

In order to gain a further insight on the pressure dependence of the structural properties of the investigated sample, the orthorhombic strains in the ab plane, $Os_{\parallel} = 2(a-c)/(a+c)$, and along the c axis with respect to the ab plane, $Os_{\perp} = 2(b/p(2)-(a+c)/2)/(b/p(2)+(a+c)/2)$, have been calculate and reported in Fig.6 for each sample. These parameter represent the deviation of the structure from an ideal cubic cell and obviously reflect the lattice parameter behaviors. Indeed, the distorted LG20 and LG30 compounds show a similar pressure dependence,

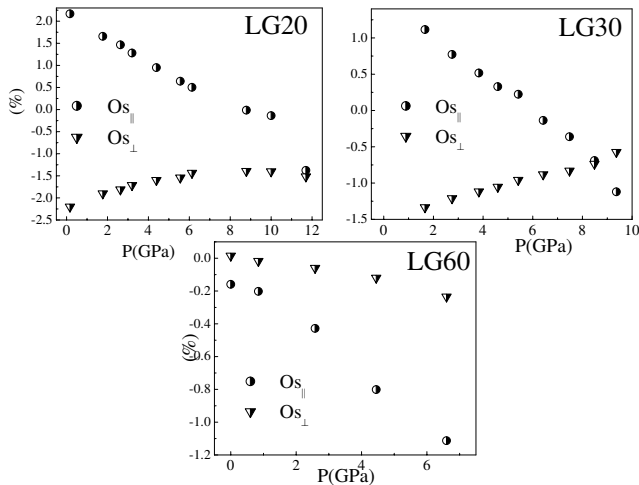


FIG. 6: Pressure dependence of orthorhombic strain in the ab plane (dots) and along the c axis (diamonds).

different from the LG60. As expected Os_{\parallel} is larger (2%) in the more distorted compound (LG20), decreases to down to zero ($a = b$) at around 8-10 GPa, where the a - b crossing is observed, and becomes negative at larger pressure. A similar behavior is observed in the LG30 Os_{\parallel} pressure dependence, but Os_{\parallel} becomes negative earlier (6-7 GPa) in this compound than in the less doped one. Opposite pressure behavior is observed for the out of plane orthorhombic distortion Os_{\perp} in both the LG20 and LG30 samples. At ambient pressure, it is negative and diminishes in absolute values with increasing pressure. Therefore, both the Os_{\parallel} and the Os_{\perp} pressure trends reveal that the application of hydrostatic pressure favors the system symmetrization in the LG20 and LG30 compounds. On the other hand, the strain pressure dependence suggests that pressure is not able to completely remove the JT octahedra distortion. Indeed, in the LG20 and LG30 compounds the structure cannot retain in the more regular phase ($Os_{\parallel}=0$, $a=b$), and the orthorhombic distortion increases in absolute value at higher pressures up to the structural transitions. In the LG60 sample, Os_{\parallel} and the Os_{\perp} have similar pressure dependence. They started from around 0 ($Pbnm$ O type structure with regular octahedra) and becomes negative as the pressure increases. Both the Os_{\perp} and the (Os_{\parallel} increase in absolute value with pressure. This phenomenon can be connected to a pressure induced octahedra rearrangement which leads to the structural transition at 7 GPa.

B. High pressure Raman spectroscopy

Raman spectra of LG20 (Ref.15), LG30 (present results) and LG60 (Ref.15) are shown in Fig.7 and Fig.8 at selected pressures. At ambient pressure, all the samples show two main phonon bands: a peak centered at around

650 cm^{-1} (ν_d) ascribed to MnO_6 octahedra stretching mode which has been demonstrated to be the the most sensitive to the extent JT distortion [17], and a peak centered at 500 cm^{-1} mostly ascribed to bending modes [15]. Looking at Fig.7, a part from the expected hard-

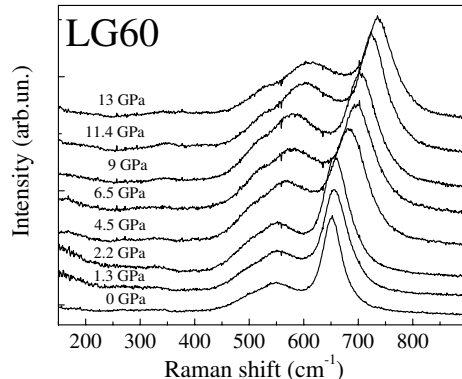


FIG. 7: Raman spectra of LG60 at selected pressure.

ening of the phonon frequencies induced by the lattice compression, no dramatic variation of the spectral shape is observed in the Raman spectra of LG60. In particular the Raman response does not appear to be sensitive to the orthorhombic to rhombohedral transition evidenced by present x-ray diffraction data between 6 and 8 GPa and discussed in the previous section. This is not surprising since the Raman spectrum of manganites is mainly due to octahedral modes which are weakly affected by the slightly different spatial arrangement of the octahedra in the two structures. An experimental confirm of the weak sensitivity of the Raman response to the orthorhombic/rhombohedral transition can be found in previous papers where the Raman spectra of both orthorhombic and rhombohedral $LaMnO_3$ are shown [27, 28]. The spectra of this compound in the two structural phases are indeed very similar, only a peak broadening and a reduction of intensity is observed in Raman spectrum of the rhombohedral $LaMnO_3$ sample with respect to the orthorhombic one [27, 28]. Bearing in mind this last result, we note that the Raman spectrum of the LG60 shows a rather abrupt peak broadening at 4.5 GPa (see Fig.7) that is at about the same pressure at which the x-ray diffraction patterns show a broadening of the Bragg peak at 15° whose splitting marks the structural transition. The Raman spectrum of the distorted LG30 sample is shown at selected pressure in Fig. 8 (a). The pressure dependence of the LG30 Raman spectrum is rather similar to that observed for the most-distorted LG20 (Ref.15) shown in Fig. 8 (b) for sake of comparison, whereas both are quite different from the pressure dependence of the LG60 undistorted compound (see Fig.7). We notice that Raman spectra of both LG30 and LG20 have been collected in orthorhombic low-pressure phase (see the previous x-ray diffraction section) thus allowing to follow the octahedral

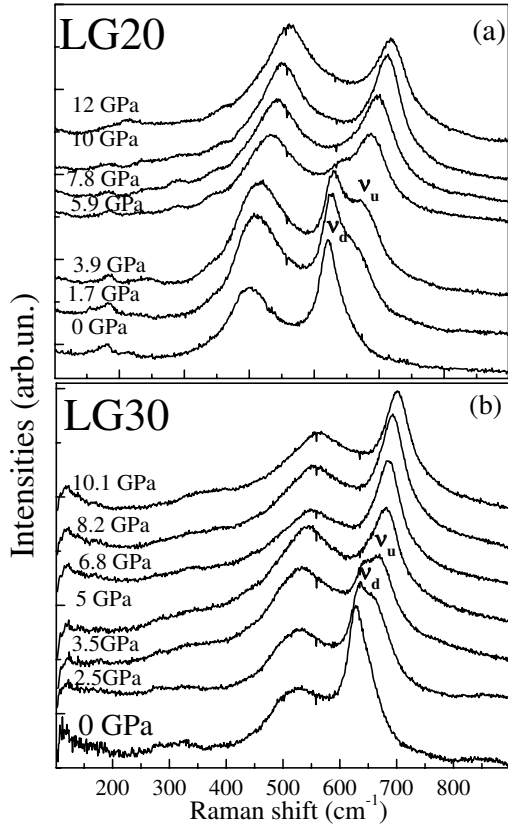


FIG. 8: Raman spectra of LG20 panel (a) and LG30 panel (b) at selected pressure.

symmetrization process. Within this context, the most important spectral feature is the appearance of a high-frequency shoulder (ν_u) of the stretching peak ν_d in the Raman spectra of both LG20 and LG30 on applying a moderate pressure. On further increasing the pressure, a progressive transfer of spectral weight from the pristine stretching peak ν_d , to the new pressure-activated peak, ν_u , occurs. This pressure-induced process extinguishes at $P=8$ GPa for LG30 and at $P=10$ GPa for LG20 when the ν_u peak only is observed. Actually the same behavior under applied pressure (appearance of a new pressure-activated ν_u peak and transfer of spectral weight), has been previously observed for the Raman spectrum of the parent compound LaMnO_3 [14]. In this case the pristine stretching peak (ν_d) still survive, albeit with a strongly reduced intensity, at the highest measured pressure (16 GPa) [14]. Nevertheless an extrapolation of the experimental data at higher pressure shows that the spectral transfer is completed at around 18 GPa [14]. This peculiar behavior has been interpreted as a signature of the octahedral symmetrization process [14, 15]. The Raman spectra of LaMnO_3 , LG20, and LG30 at ambient pressure show a single ν_u peak ascribed, as mentioned above, to the octahedral stretching mode of distorted octahedra (ν_d). The appearance of the new ν_u peak on applying the

pressure is thus ascribed to the onset of domain of undistorted or less-distorted octahedra with a slightly higher stretching frequency ν_u . The pressure induced transfer of spectral weight from ν_d to ν_u is thus simply the spectral evidence of a pressure-induced conversion of distorted octahedra into regular ones [15].

It is particularly interesting to compare the pressure behavior of the ν_d to ν_u stretching peaks obtained for the three samples reported in the present paper and for the LaMnO_3 [14] as shown in Fig. 9. On applying pressure, the new ν_u peak in the LaMnO_3 , LG20, and LG30 spectrum appears at about the same frequency of the stretching phonon of LG60 and, after the completion of the spectral weight transfer the highest frequency peaks of the three samples show about same pressure dependence. Bearing in mind that the LG60 lattice consists of regular octahedra only and that the onset and the completion of the symmetrization process occurs at pressure which decreases on decreasing the extent of JT distortion (i.e on going from LaMnO_3 to LG20 to LG30) the comparative analysis of the pressure behavior of the ν_d to ν_u peaks strongly support their assignments to stretching modes related to distorted and undistorted (less-distorted) octahedra [15]. The simultaneous occurrence of both the

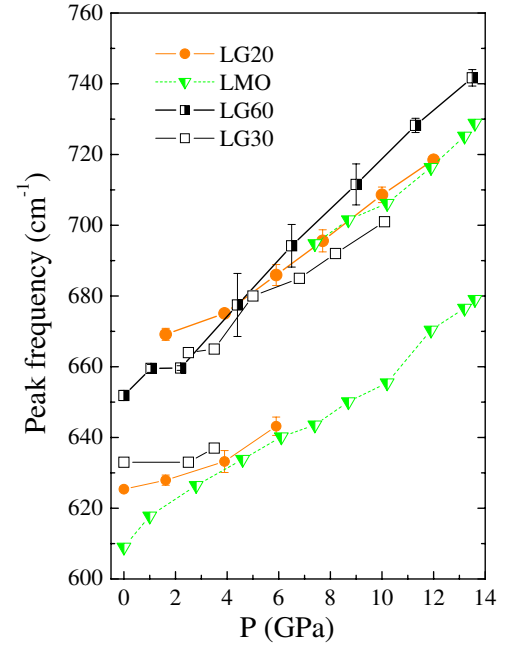


FIG. 9: Pressure dependence of the ν_d and ν_u stretching frequencies of LaMnO_3 (Ref. 14), LG20 and LG30 compared with that of the stretching frequencies of the LG60.

ν_d and ν_u peaks within certain pressure ranges depicts a phase separation scenario, where two kinds of MnO_6 octahedra are simultaneously present. At intermediate pressures, the coexistence of domains of distorted and

more regular octahedra can be clearly claimed for both the LG20 and LG30 compound and this finding can be obviously extended to the LaMnO_3 case previously investigated [14]. The analysis of the Raman measurements thus confirms the results discussed in the previous x-ray diffraction section and adds further and more detailed information about the symmetrization process, not revealed by the high pressure diffraction measurements.

IV. DISCUSSION AND CONCLUSION

The analysis of the high-pressure X-ray diffraction data shows that all the three investigated samples undergo a pressure induced transition from the orthorhombic $Pbnm$ phase towards structures with higher symmetry. The three samples at ambient pressure show a different extent of octahedral JT distortion which decreases going from LG20, to LG30, and to LG60, where the octahedra are not distorted. The transition pressure to the higher symmetry phase progressively decreases on reducing the extent of JT distortion being $P=12$ GPa for LG20, $P=10$ GPa for LG30, and $P=7$ GPa for LG60. The high-pressure phase is a more symmetric orthorhombic structure ($Imma$) for the most distorted sample, LG20, whereas LG30 and LG60 enter the rhombohedral ($R\bar{3}c$) phase. This results clearly indicate a key role of the JT distortion in stabilizing the manganite structures. Moreover, the pressure dependence of the structural parameters obtained from the two samples (LG20 and LG30), distorted at ambient pressure, clearly demonstrates that the most important structural effect of pressure is that of reducing the octahedral distortion. The last finding is confirmed by the analysis of the Raman data. In particular a pressure induced transition from a distorted octahedral configuration to a more regular one at high pressure is well evident in the observed pressure dependence of the Raman-active stretching modes of LG20 and LG30. Moreover the peculiar pressure behavior shown by the Raman spectra of LG20 and LG30 depicts a phase separation scenario. On applying a moderate pressure a second stretching peak associated to the onset of domains of less distorted octahedra appears in the Raman spectra. On further increasing the pressure, the number and/or the extension of the distorted octahedra domains is progressively reduced down to zero and after the completion of this process the structural transitions to more symmetric phases occur. The simultaneous presence of two stretching peaks associated to distorted and less distorted octahedra at intermediate pressure is thus the clear signature of a phase separation regime. Basing on the present results and using those reported in Ref. [14] and in ref.[32] for LaMnO_3 , in Ref. [26] for LaGaO_3 and those for from Ref. [10] for ambient pressure data, the pressure vs. Ga-concentration phase diagram shown in Fig. 10, can be drawn. From the figure it is well evident that the transition pressure to the higher symmetry phases (orthorhombic $Imma$ and rhombohedral $R\bar{3}c$) de-

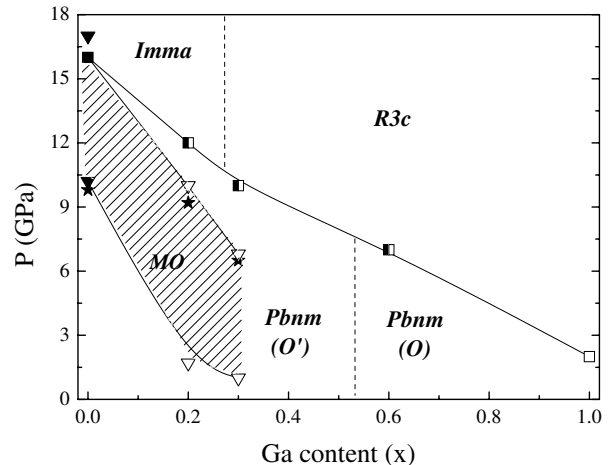


FIG. 10: P vs Ga-concentration phase diagram. Black square and triangles: X-ray and Raman results on LaMnO_3 from ref. [14]; white square: X-ray results on LaGaO_3 from ref. [33]; black and white squares and white triangles: X-ray and Raman present data, respectively. The stars indicate the pressure where the a - b lattice parameter crossing occurs. MO= Mixed Octahedra.

creases as the Ga content increases. Therefore, the more symmetric phases appear to be promoted by the octahedra symmetrization induced by the Ga content. The region, where the symmetrization process occurs through the onset of domains of less-distorted octahedra as obtained by present measurements and from those reported in Ref. [14] is also shown in Fig. 10. In the same figure, the pressures at which the a - b crossing for LG20 and LG30 (present data) and for LaMnO_3 (Ref. [14]) is observed, are also reported. This behavior is clearly strictly connected to the symmetrization process and it can be reckon as a general indication of the onset of a structural instability in the perovskite structure of manganites which anticipates a structural transition. This result thus suggest that a pressure induced transition of the system from the orthorhombic to the cubic structure appears to be very unlikely.

Although a pressure induced symmetrization process in LG20 and LG30 as well as in LaMnO_3 (Ref. 14) is clearly revealed by both x-ray diffraction and Raman measurements the complete suppression of the JT distortion in the high-pressure phases cannot be claimed. Indeed, the pressure-driven symmetrization process certainly suppresses the *coherent* JT distortion in the higher symmetry phases $Imma$ (LG20) and $R\bar{3}c$ (LG30) but the occurrence of incoherent and/or dynamic MnO_6 JT distortion cannot be excluded. Finally indications on the orbital ordered state in the high pressure phases can be inferred from the analysis of the pressure dependence of the lattice parameters and cell volumes. Above the structural transition, the occurrence of orbital disordered

state can be claimed for the rhombohedral LG30 sample, whereas in the orthorhombic *Imma* LG20 the persistence of some kind of orbital orientation cannot be ruled out, but the occurrence of a specific orbital configuration seems to be able to bring into question by the bulk modulus values obtained with a Birch-Murnaghan curve. In conclusion the present measurements provide a wide characterization of the pressure behavior of three representative compounds belonging to the $\text{LaMn}_{1-x}\text{Ga}_x\text{O}_3$ family and allow to draw a first sketch of the P vs. Ga-content phase diagram. The obtained results provide also several general structural indications which can be ex-

ploited in studying the effect of the chemical pressure in other manganite systems at ambient pressure. Although open questions about the effect of lattice compression on the persistence of some kind of octahedral distortions and on the orbital ordering still remain, the present data represent a fundamental base for extending to this family of compounds the advanced theoretical studies carried out on the parent LaMnO_3 . Finally, to gain a deeper insight on the effect of lattice compression, high-pressure neutron studies on these compound would be necessary to investigate the effects of lattice compression on the magnetic ordering.

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